TITLE: Interface Conduction between Conductive ReO3 Thin Films and NdBa2Cu3O6 Thin Film

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Interface Conduction between Conductive ReO_3 Thin Film and $NdBa_2Cu_3O_6$ Thin Film

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ABSTRACT

The Re oxide films were deposited on quartz glasses by RF reactive sputtering from a Re metal target. The lowest resistivity was observed in the film *in-situ* annealed at 200°C in Ar atmosphere and showed the order of 10^{-4} Ωcm of which the value was still about 10 times as large as that of a single crystal ReO_3. The temperature dependence of the resistivity revealed a metallic behavior. A superconductivity did not take place in the bilayered film of ReO_3 / $NdBa_2Cu_3O_6$. In the interface region the resistivity minimum probably caused by the Kondo effect was observed in the neighborhood of 120K.

INTRODUCTION

Most high-*Tc* cuprates superconductors have two-dimensional multilayered structures with CuO_2 planes. The cuprates show superconductivity when enough carriers are doped to the CuO_2 planes from a charge reservoir block (CRB). We have been interested in rhenium (Re) oxides [1] as the candidate of a CRB because multi-valences, +2 ~ +7, of Re ions are noticeable in various Re oxides. We propose the multilayered films with ReO_3 (CRB) and cuprates superconductors in order to synthesize novel high-*Tc* superconductors. Especially an infinite layered cuprates is expected to become the candidate of the pair material for Re oxides.

It is well known that the ReO_3 reveals extremely high conductivity comparable to that of Ag. The structure of ReO_3 is simple as shown in Figure 1. It was, however, difficult to obtain Re oxide films due to vigorous sublimation at comparatively low temperature.

The purposes of this work are to prepare the Re oxide thin films and to study the resistivity of the ReO_3 thin film, and to evaluate it as the material of a CRB. As a preliminary research we

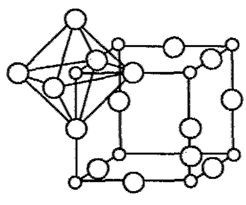

Figure 1. The structure of ReO_3.

have carried out the deposition of ReO_3 thin films on reduced nonsuperconductive $NdBa_2Cu_3O_6$ films, and discussed the transport properties of the bilayered film.

EXPERIMENTAL

We prepared the rhenium oxide thin films by reactive RF sputtering from the targets which were compressed Re powder or a metal Re disk. The substrates were quartz glasses. The distribution of temperature on the substrate was kept constant and uniform by using a copper sheet between the substrate and its holder. The RF electric power was about 100 W. The reactive and sputtering gases were O_2 and Ar, respectively. The pressure of the gas was Ar / O_2 = 90 / 10 mTorr. The substrate temperature was changed from ambient to 240°C. In the case of ambient, the prepared films were *in- situ* annealed in the temperature range from 150°C to 300°C for 30 minutes after the film deposition.

Superconductive $NdBa_2Cu_3O_7$ films were prepared by a pulsed Laser ablation deposition. The detailed preparation conditions will appear elsewhere. The deposition of ReO_3 was carried out on the reduced nonsuperconductive $NdBa_2Cu_3O_6$ film. The deoxidization of the $NdBa_2Cu_3O_7$ thin film was carried out by the annealing at 300°C in a vacuum. By deoxidization in the vacuum the lattice parameter **c** of the $NdBa_2Cu_3O_{7-\delta}$ thin film changed from 11.73Å to 11.86Å. The **c** value after the annealing was almost equivalent to that of $NdBa_2Cu_3O_6$.

The crystal structure of the films was analyzed by reflected x-ray diffraction (XRD). The surface of film was observed by a scanning electron microscope (SEM). The resistivity was measured by a four-probe technique. The current value was set up so that changes of the voltage by the noise came within about 1% of measurement voltage values.

RESULTS & DISCUSSION

The Re oxide films did not grow on the substrates at substrate temperatures above 100°C because of the strong sublimation of Re oxides. It was quite difficult to control a suitable substrate temperature in order to obtain the film.

The deposited films on ambient substrates deliquesced in air and were yellow in color. These properties were consistent with the features of Re_2O_7. The film was amorphous, which was confirmed by XRD. Then, post annealing was done in order to proceed with the crystallization and reduction of as-prepared films.

The prepared films were annealed in Ar atmosphere in the temperature range from 150°C to 300°C for 30 minutes. Figure 2 shows the typical XRD spectra of the annealed films. The peaks observed were assigned as those of the ReO_3 phase.

Figure 3 shows the peak intensity ratio of ReO_3 (100) / ReO_3 (110) and the full width at half maximum (FWHM) as a function of annealing temperature. The peak intensity ratio is about 7 at annealing temperatures above 200°C, while it is less than 2 at the annealing temperature of 150°C. The FWHM reveals the minimum value, 0.15° in the film annealed at 220°C.

The crystal growth at 150°C was low probably because of the poor reduction of Re_2O_7. When the annealing was carried out above 200°C the films changed to ReO_3 films with the preferential orientation of (100) planes.

Figure 4 shows the annealing temperature dependence of color change of Re oxides. The color of ReO_3 changed from blue to green with increase of annealing temperature. It is thought that the degree of oxidation of ReO_3, which changed slightly by annealing temperature, influenced the color of the films.

Figure 5 shows the typical resistivities of thin films with the ReO_3 phase as a function of temperature. The resistivity slightly decreases with decreasing temperature. Metallic behavior was observed in the all annealed films. The film annealed at 260°C shows a

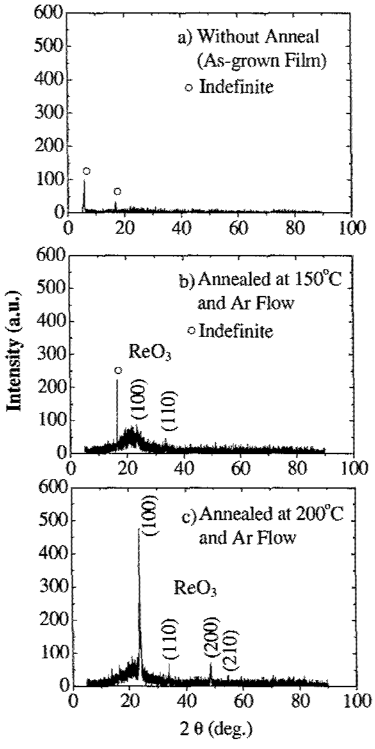

Figure 2. XRD spectra.

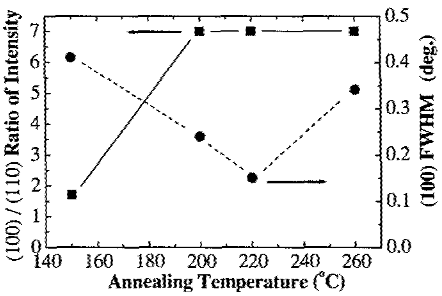

Figure 3. Annealing temperature dependence of the intensity ratio of $ReO_3(100)/(110)$, and the full width at half maximum.

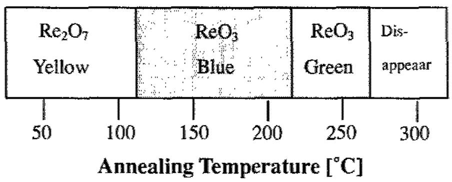

Figure 4. Annealing temperature dependence of color changes of Re oxides.

comparatively high resistivity. This was thought to be caused by the decrease of the degree of the oxidation.

In Figure 6 the room temperature resistivity are summarized with the change of annealing temperature. In the annealing temperature range from 200°C to 260°C, the resistivity of the films increases as the annealing temperature increases. Then the crystallinity decreased as indicated by the increase of FWHM in the temperature range of 220 ~ 260°C. The ReO_3 film may be changing to form a more reduced, lower conductivity phase as shown by the decrease in conductivity.

Conclusively, the optimum annealing condition to obtain conductive ReO_3 thin films was at around 200°C. The resistivity of the single-crystal bulk ReO_3 was very low [2], 10^{-5} to 10^{-7} Ω cm, and showed metallic conduction with a large resitivity ratio, R (300K) / R (100K) of about 10. The resistivity of the ReO_3 film was, however, still several ten times larger than that of the single crystal. The higher crystallinity and the optimum oxidation are indispensable in order to acquire the higher conductivity.

Figure 7 shows the SEM photograph of the cross section of the ReO_3 film on the quartz glass. It was confirmed that the ReO_3 film was deposited and grown uniformly on the substrate. Therefore we can discuss a transport phenomenon in the interface of the film and the substrate.

The bilayered film with $NdBa_2Cu_3O_6$ and ReO_3 was studied in order to investigate the doping effect from ReO_3 to the nonsuperconductive cuprate layer. The resistivity of $NdBa_2Cu_3O_6$ in the room temperature became about 10^3 times as large as that of the ReO_3 thin film. For this reason, the resistivity on the surface of a bilayered film is dominated by the resistivity of the ReO_3 thin film.

Figure 8 shows the resistivity of ReO_3 thin film and the bilayered film. The superconductivity expected in the temperature range above 77K was not observed. The value and the temperature dependence of the resistivity are almost the same as those of the ReO_3 thin

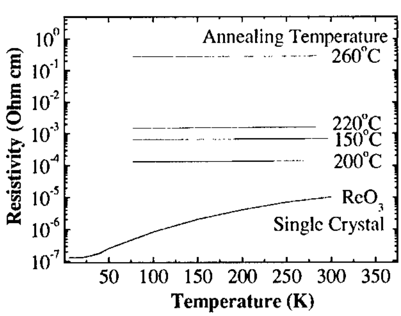

Figure 5. The temperature dependence of resistivity of ReO_3 thin films, and single crystal [2].

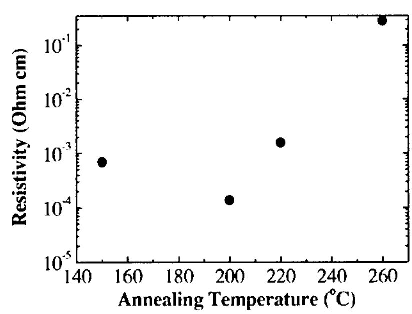

Figure 6. The change of the 300K resistivity depending on annealing temperature.

film. It should be, however, noticed that the "resistivity minimum" appeared at a temperature of about 120 K. It is believed that the spins of the $NdBa_2Cu_3O_6$ influences the resistivity of the ReO_3 in the near the interface. When the spin reorientation takes place corresponding to the antiferromagnetic phase transition of the $NdBa_2Cu_3O_6$ film, the resistivity observed may be changed. The resistivity minimum is expected appear at the temperature below a Néel temperature.

As is well known with respect to the Kondo effect [3], the magnetic impurities in metals establish the resistivity minimum. In the present case, it is possible that the antiferromagnetic ordering of spins produces the same phenomenon. We think that scattering of conductive electrons are influenced by the magnetic moments through Kondo effect in the interface of the bilayered film. The order-disorder of magnetic moment of Cu strongly is related to the appearance of high temperature superconductivity. The results observed in the interface of the bilayered film give us a novel material system to investigate mechnaisms of a high temperature superconductivity.

CONCLUSIONS

Since Re oxides are easily sublimed, it was difficult to obtain the as-grown ReO_3 film. The ReO_3 thin film was prepared by adopting a post-annealing process. The crystal growth of the ReO_3 phase and preferential (100) orientation depended on the annealing temperature. The metallic conductivity of the ReO_3 thin film was confirmed for the first time. From the influences of crystallinity and the degree of reduction, a higher conductivity ReO_3 thin film was obtained by post-annealing at about 200°C. The expected superconductivity was not observed

Figure 7. The SEM photograph of the cross section of the ReO_3 film on the quartz glass.

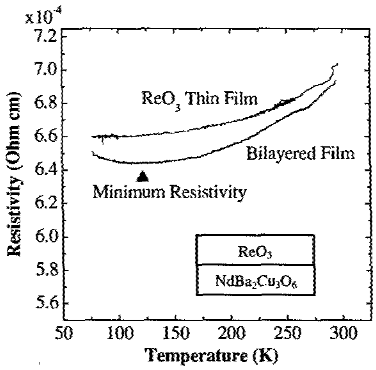

Figure 8. The temperature dependence of the resistivity of the bilayered film

in the bilayered ReO_3 / $NdBa_2Cu_3O_6$ thin film. On the other hand, the resistivity minimum appeared in the bilayered film. Therefore, we conclude that the interesting interface phenomenon which takes place in the conductive electron systems strongly depends on spin ordering.

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Fracture and Mechanical Properties III